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THE DETERMINATION OF THE NICKEL-ELECTRODE CAPACITY FROM THE DROP IN POTENTIAL AFTER TURNING OFF THE POLARIZING CURRENT

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THE DETERMINATION OF THE NICKEL-ELECTRODE CAPACITY FROM THE DROP IN POTENTIAL AFTER TURNING OFF THE POLARIZING CURRENT

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ABSTRACT. The initial part of the potential drop curve recorded within a specified time after turning off the polarizing current is used in determining the capacity of a nickel electrode. An oscillographic apparatus, the operation of which is described, is used. The results of the tests indicate that the capacity of the electrode is independent of potential for a given polarizing current and that capacity is constant within the specified period of time. The results are also in agreement with the experimental results of several other investigators, with the theory that hydrogen atoms are not adsorbed on the surface of a mercury cathode in significant quantities and with the theory that the potential drop of the cathode after the polarizing current is turned off is a function only of the discharge of ions from a binary-layer. The nickel electrode was tested in H_2SO_4 and NaOH solutions. The experimental procedures are described and figures and various reactions are furnished.

A method of determining the capacity of an electrode on the basis of the drop in potential after switching off the polarizing current characterizes the state of the surface of the electrode with the flow of current. /1050*

Of particular interest in the determination of electrode capacity is the initial part of the curve of potential drop obtained after time interval t which satisfies the condition: $2.3\, i_0 t \ll Cb$, where i_0 is the strength of the polarizing current, C is the capacity of the electrode, and b is a coefficient in Tafel's equation [1].

Hickling and Salt [2] managed to determine the electrode potential within $2 \cdot 10^{-5}$ seconds after switching off the current. An oscillographic apparatus, by which it is possible to measure electrode potential within $5 \cdot 10^{-5}$ seconds after turning off the current, was used in the experiment of N. A. Fedotov [3] for determining the capacity of a mercury cathode on the basis of the curves of potential drop.

In our experiment we used an improved oscillographic apparatus, which V. I. Protserov helped to design, for measuring the drop in potential.

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* Numbers in the margin indicate pagination in the foreign text.

The measurement process consists of the following. When the switch of the oscillograph is pressed the scanning of a phenomenon in time is actuated and the potential of the electrode under examination relative to an electrode selected for comparison is transmitted to the input of the oscillograph. This corresponds to the initial horizontal part of the curve on the screen of the oscillograph. The polarizing current is cut off for about 1/10 of the scanning duration and the potential of the electrode changing in time is transmitted to the input of the oscillograph. The path of the beam on the screen of the oscillograph is photographed; the oscillogram obtained is deciphered using a measuring microscope.

The curve of potential drop consists of a series of points which determine the time scale (time marks). The distance between the marks can be made to equal 10^{-5}, 10^{-4}, or 10^{-3} seconds. The axis of the potentials is calibrated by transmitting a precisely known amplitude of alternating current to the input of the oscillograph from a potentiometer. A four-stage amplifier with an input impedance of 100 MΩ at maximum amplification produces a vertical image 1 cm in length per 1 mv of potential on the screen of the oscillograph. The oscillograph is powered by alternating current by means of a power unit.

The operation of the apparatus is checked by measuring the voltage drop of a discharging capacitor in the circuits equivalent to the cell with a time constant from $CR_1 = 10^{-1}$ to $CR_1 = 1.5 \cdot 10^{-4}$ second. (C is the capacity of the capacitor and R_1 is the parallel resistance with the series resistance not exceeding the parallel resistance $R_1 \geq R_2$). The results of these measurements led us to conclude that the error in the determination of capacity under various conditions of vertical amplification and scanning velocity (within the interval of t from 10^{-5} to 10^{-2} seconds) does not exceed ± 4%.

The electrode capacity is computed by a formula which establishes the relationship between the drop of over-voltage ($\Delta\eta$), time after interruption of the current (t), strength of the polarizing current (i_0) and electrode capacity (C):

$$\Delta\eta = b \lg\left(1 + \frac{2{,}3\, i_0 t}{Cb}\right). \qquad (1)$$

In deriving the equation (1) it was assumed that the value C becomes constant /1051 in the specified range of values of η.

For the purpose of further checking the operation of the apparatus, as well as for determining the capacity of the mercury electrode in a wider range of current densities (10^{-5} - 10^{-1} a/cm^2) than was done in the experiment of N. A. Fedotov [3], measurements were made of the capacity of an amalgamated copper wire electrode in a 1 N solution of H_2SO_4.

The results obtained show that the capacity of the cathode is independent of the potential in the specified range of densities of the polarizing current

within the limits of accuracy of the given method, and that the capacity is constant in time within the specified interval of t from 10^{-5} to $3 \cdot 10^{-3}$ sec. The values found for capacity varied within the limits of 17 - 19 $\mu F/cm^2$, which is in agreement with the data of other authors [3,4]. These results are in agreement with the theory that hydrogen atoms are not adsorbed on the surface of a mercury cathode in quantities sufficient to be measured by the specified method and that the potential drop of the cathode after the current has been switched off is determined only by the discharge of ions of a binary electrical layer.

Measurements with a nickel cathode were conducted in 1 N H_2SO_4 and 0.65 - 0.8 N NaOH solutions in 1 atmosphere of hydrogen. The preparation of the surface of the electrode is very important. After being cleaned with a fine glass powder and scoured, the nickel electrode (a sheet of spectrally pure nickel with a visible surface of 0.2 - 0.5 cm^2) was calcinated in a current of hydrogen at 420° directly within the measuring cell and was immersed in the solution without being exposed to the air.

In a 1 N solution of H_2SO_4 the capacity for high densities of polarizing current (10^{-1} a/cm^2), which is calculated on the basis of the first points of the curve of the drop which correspond to the time t = 10^{-5} - 10^{-4} sec., amounts to 20 - 25 $\mu F/cm^2$ of visible surface. As the density of the current decreases the capacity of the electrode increases to 50 - 55 $\mu F/cm^2$ for $i_0 = 3 \cdot 10^{-5}$ a/cm^2. Figure 1 expresses the dependence of the initial capacity of a nickel cathode on the over-voltage in a 1 N solution of H_2SO_4.

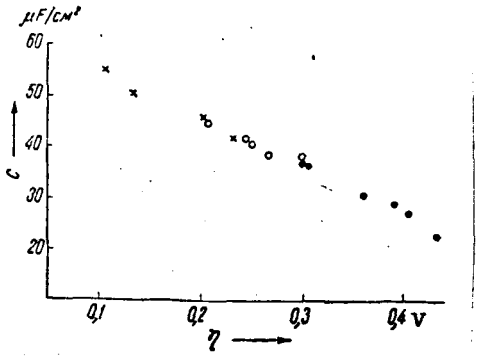

Fig. 1. Dependence of the Capacity of Nickel Electrode in 1 N Solution of H_2SO_4 on Over-Voltage η. Capacity is Calculated from the First Part of the Curve of Potential Drop after the Polarizing Current is Switched Off. The Various Designations Refer to Different Experiments.

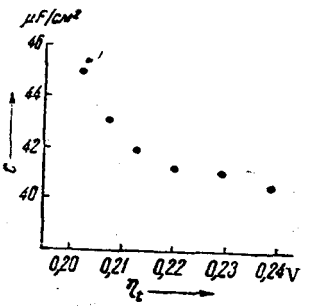

Fig. 2. Dependence of the Capacity of a Nickel Electrode in a 1 N Solution of H_2SO_4 on Over-Voltage η_t. Values of Capacity are related to time t = = (5; 10; 15; 20; 25; 30)·10^{-4} sec. after the Current has been Switched Off.

Figure 2 shows the change in capacity of a nickel cathode according to the curve of potential drop. The data for the various moments of time after the current has been turned off indicate an increase in capacity with a reduction in the potential of the electrode along the curve of drop. Since the value of C in this case does not become constant in time, equation (1) is applicable for the curve of drop as a whole. But it is applicable in the first approximation for a small segment of the curve.

We observed an analogous increase in the capacity of a nickel electrode with time t and also an increase in the capacity with a reduction of cathode potential, starting with 20 - 25 $\mu F/cm^2$ (for $i_0 \sim 10^{-1}$ a/cm^2) to 70 - 80 $\mu F/cm^2$ (for $i_0 = 3 \cdot 10^{-4}$ a/cm^2) in an alkaline solution. In the experiment of P. D. Lukovtsev and S. D. Levina [5], who measured the potential drop of a nickel electrode in alkaline solutions visually after periods calculated in seconds, a significant decrease in the capacity with time was also observed after the polarizing current was switched off. /1052

The minimal values of capacity 20 - 25 $\mu F/cm^2$ observed can be regarded as similar to the values of a binary-layer capacity; in other words the initial part of the curve of potential drop is apparently related only to the discharge of ions of a binary electrical layer which flows according to the reactions: $H^+ + e \rightarrow H_{ads}$, and $H^+ + e + H_{ads} \rightarrow H_2$. Because of the values of 17 - 19 $\mu F/cm^2$ for a completely smooth surface, the values which we obtained for the capacity appear to be somewhat underestimated (we did not determine the coefficient of roughness, but it was probably not less than 1.5). In several experiments of other authors [6,7], however, even lower values than should be expected were obtained for the capacity of solid electrodes (including nickel) measured using alternating current, judging by the value of 16 - 18 $\mu F/cm^2$ for the mercury electrode. It may be assumed that the microrelief of the solid surface has some effect here. The effective part of the surface of the electrode is reduced when the current has high densities. As a consequence of the resistance drop in the pores and microcavities the latter are not involved in the propagation of the current. Therefore the effective surface of the electrode is approximately equal to the visible surface. The presence on the electrode of adsorbed hydrogen may also result in some reduction of the binary-layer capacity [8]. It is felt that the unambiguous solution of these problems is not possible within the framework of the method under consideration.

The increase in capacity by measure of the reduction of the over-voltage indicates the presence on the surface of the nickel cathode of adsorbed electrochemically active hydrogen which enters into the reaction according to the equation: $H_{ads} \rightarrow H^+ + e$, resulting in the deceleration of the drop in potential and an increase in the capacity of the electrode as calculated on the basis of the curve of potential drop. If a large part of the surface of the electrode were covered with adsorbed hydrogen which could achieve equilibrium in the solution under the conditions of the experiment, the

magnitude of capacity would have to be 1000 - 2000 $\mu F/cm^2$. Thus the results obtained by us show that for values of η exceeding 100 mv for a 1 N solution of H_2SO_4, and exceeding 150 mv for a solution of NaOH, the electrochemically active hydrogen, i.e. capable of being ionized at these potentials, occupies only a small part of the surface (for values of η exceeding 400 mv for H_2SO_4 and exceeding 550 mv for NaOH, as we have shown, this cannot be achieved by the method under consideration).

The measurements of the capacity of an iron cathode according to the curves of potential drop in a 1 N solution of H_2SO_4 yielded values of 40 - 60 μF per cm^2 of visible surface. For the iron electrode in an alkaline solution (1 N NaOH) we obtained even higher values for capacity. At relatively high cathode potentials (η = 550 mv) the capacity of the electrode, as calculated on the basis of the first points of the curve of potential drop, amounts to 150 - 200 $\mu F/cm^2$ and sharply increases with time after the interruption of the current.

In conclusion we wish to express our heartfelt gratitude to Academician A. N. Frumkin for his attention and advice rendered during the completion and consideration of these experiments.

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